

- <sup>1</sup> Baeyer, *Ann. Chem.*, **127**, 200 (1863); **130**, 140; **131**, 292 (1864).
- <sup>2</sup> Ceresole, *Ber. chem. Ges.*, **16**, 1133 (1883).
- <sup>3</sup> Behrend and Roosen, *Ann. Chem.*, **251**, 235 (1889).
- <sup>4</sup> Biltz and Paetzold, *Ann. Chem.*, **433**, 64 (1923).
- <sup>5</sup> Davidson and Baudisch, *J. Biol. Chem.*, **64**, 619 (1925).
- <sup>6</sup> Hantzsch and Isherwood, *Ber. chem. Ges.*, **42**, 986 (1909); Hantzsch and Issaias, *Ibid.*, 1000.
- <sup>7</sup> Traube, *Ber. chem. Ges.*, **33**, 1371 (1900); *Ann. Chem.*, **432**, 266 (1923).
- <sup>8</sup> Biltz, Heyn and Bergius, *Ann. Chem.*, **413**, 68 (1916).
- <sup>9</sup> Wheeler and Johnson, *J. Biol. Chem.*, **3**, 183 (1907).
- <sup>10</sup> Gregory, *J. prak. Chem.*, [1], **32**, 278 (1844), showed that dialuric acid gave a white precipitate with barium ion, but that it was readily oxidized by air to alloxantine, which gave a purple precipitate. The role of air in the formation of a purple barium salt from dialuric acid was also appreciated by Liebig and Wöhler, *Ann. Chem.*, **26**, 279 (1838). For a modern interpretation of the color of barium alloxantinate, see Hantzsch, *Ber. chem. Ges.*, **54**, 1267 (1921) and Retinger, *J. Am. Chem. Soc.*, **39**, 1059 (1917).
- <sup>11</sup> Davidson and Baudisch, loc. cit.
- <sup>12</sup> Traube, loc. cit. Levene and Senior, *J. Biol. Chem.*, **25**, 607 (1916).
- <sup>13</sup> Clarke and Kirner, *Organic Syntheses*, **2**, 49 (1922).
- <sup>14</sup> Biltz, Heyn and Bergius, loc. cit. Ceresole, loc. cit.

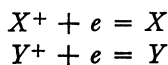
## CONCENTRATION OF THE $H^2$ ISOTOPE OF HYDROGEN BY THE FRACTIONAL ELECTROLYSIS OF WATER\*

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Communicated June 10, 1932

If the reactions



are both possible cathodic reactions, the one having the lower cathodic potential will be favored to the practical exclusion of the other during an electrolysis under equilibrium conditions. Though the normal electrode potentials of the isotopes of all elements except hydrogen must be so nearly the same that no appreciable separation can be expected from any small differences, this may not be true in the case of the hydrogen isotopes because of the very large mass ratio.

In addition to a possible small difference in the normal electrode potentials of these two isotopes, the mechanism of the formation of hydrogen gas at the cathode involves the diffusion of the two species of ions through the cathode film and the subsequent union of the discharged ions to produce hydrogen molecules, in both of which processes (differences in "polari-

zation") there exists the possibility of a fractionation of the mixture, probably with a resulting enrichment of the residual water in respect to  $H^2$ , the species present at the smaller concentration. In that case it is obvious that a systematic fractionation by electrolysis should lead to two final fractions consisting, respectively, of (1) pure  $H^1$  and (2) the equilibrium (i.e., electrolysis equilibrium) mixture of  $H^1$  and  $H^2$ . It is impossible to predict the composition of this equilibrium mixture. While it might conceivably consist of almost pure  $H^2$ , it will probably be found to contain the  $H^2$  isotope in a certain maximum concentration beyond which, practically speaking, it will not be possible to go.

On the basis of the above reasoning it appeared possible to concentrate the  $H^2$  isotope of hydrogen by the electrolysis of water, and such an experiment was started at the Bureau of Standards on December 9, 1931. This experiment is still in progress and it is planned to compare the physical properties of the residual water with those of ordinary water and also to examine both the hydrogen and the oxygen of the residue, since some concentration of  $O^{18}$  as well as of  $H^2$  appears possible.

Meantime, it seemed worthwhile to examine some of the residues obtained from the commercial electrolysis of water for the production of oxygen, although the conditions under which commercial cells are operated are rather unfavorable, owing to the continual additions of fresh water to the cells. Through the courtesy of the Southern Oxygen Company of Alexandria, Va., and later of the Ohio Chemical Company of New York, samples of the residual solutions from cells continuously operated for two and three years, respectively, were secured. The hydrogen and oxygen from this water have been examined at Columbia University.

The hydrogen was examined spectrographically as described by Urey, Brickwedde and Murphy.<sup>1</sup> No quantitative estimate of the abundance of  $H^2$  can be made by this method, but the photographs show that there is a very definite increase in the abundance of  $H^2$  relative to  $H^1$  in these residual solutions.

The oxygen was combined with nitrogen to form nitric oxide and any change in the relative abundances of the oxygen isotopes was estimated from the relative intensities of the absorption bands of the molecules  $O^{16}N^{14}$  and  $O^{18}N^{14}$  using ordinary nitric oxide for comparison.<sup>2</sup> The oxygen analysis indicated a decrease of about 8 per cent in the concentration of  $O^{18}$  but the uncertainty in the estimation is about this large and therefore the change cannot be regarded as significant.

The above results are of great importance for we now know that there are large quantities of water in these electrolytic cells containing  $H^2$  in relatively high concentrations and also there is available now a method for concentrating this isotope in large quantities.

In selecting from the determination in the literature, a value for the

relative abundances of  $H^1$  and  $H^2$  in natural terrestrial hydrogen, it is now necessary to know the past history of the hydrogen sample used by the observer and some of the discrepancies reported may be due to differences in the samples used.<sup>3</sup>

In addition to the electrolysis method for fractionating water, the distillation method could also be utilized by the unidirectional evaporation of a saturated brine at a sufficiently low temperature. While the theoretical efficiency of the process is less than that for the evaporation of liquid hydrogen itself, the experimental technique is much simpler and the process could be operated continuously with very little attention.

Various heterogeneous chemical reactions suggest themselves also as methods for securing fractionation of the two isotopes. Thus treatment of a large quantity of hydrochloric acid with iron or zinc should lead to a concentration of the  $H^2$  isotope in the undecomposed residual acid.

\* Publication approved by the Director of the Bureau of Standards of the U. S. Department of Commerce.

<sup>1</sup> Harold C. Urey, F. G. Brickwedde and G. M. Murphy, *Phys. Rev.*, **39**, 164 (1932); **39**, 536 (1932).

<sup>2</sup> See a forthcoming paper by G. M. Murphy and Harold C. Urey for experimental details.

<sup>3</sup> R. T. Birge and D. H. Menzel, *Phys. Rev.*, **37**, 1669 (1931); Walter Bleackney, *Phys. Rev.*, **39**, 536 (1932); Harold C. Urey, F. G. Brickwedde and G. M. Murphy, *Phys. Rev.*, **40**, 464 (1932); Kallman and Lazareff, *Naturwiss.*, **12**, 206 (1932).

## THE ELECTRONIC STRUCTURE OF THE NORMAL NITROUS OXIDE MOLECULE\*

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Communicated June 10, 1932

In a recent note<sup>1</sup> I applied a table of atomic radii for use in covalent molecules in predicting values of the moment of inertia of nitrous oxide, assuming various structures for the normal state. The values given are the following:

$$\begin{array}{rcl}
 \begin{array}{l}
 :\ddot{N}::N::\ddot{O}: \\
 :N:::N::\ddot{O}: \\
 :\ddot{N}:N:::O:
 \end{array}
 &
 \begin{array}{l}
 75.8 \\
 75.3 \\
 75.2
 \end{array}
 &
 \left. \begin{array}{l} \\ \\ \end{array} \right\} 66.7 \left. \begin{array}{l} \\ \\ \end{array} \right\} 58.1 \times 10^{-40} \text{ g. cm.}^2
 \end{array}$$